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FIRST QUARTERLY PROGRESS REPORT

DEVELOPMENT OF PACKAGE DECONTAMINATING SYSTEM

(July through September 1971)

by

G. A. Richardson

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FOREWORD

This First Quarterly Progress Report was authorized under Task 1B662710AD6002, "Development of Package Decontaminating System." The research described herein was accomplished during the quarter beginning 1 July 1971 and ending 30 September 1971.

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DIGEST

The objective of this research effort is to study means of improving the present operational decontaminant DS2. An improved system and the most desirable would include a reduction of toxicity, and fuming while improving low temperature viscosity and reactivity. In addition, an improved system would be effected by reducing the number of constituents while simultaneously retaining the present decontaminating capability.

This initial quarter of effort began with a visit to Edgewood Arsenal: To establish contact with technical personnel, to survey the recent development in decontamination, and to confirm the objectives of the program.

Procedures, analytical instruments, techniques etc., were reinitiated.

Preliminary experiments were conducted using crown ether/KOH, carbowax/KOH, and aprotic/alkali halide systems. The crown ether/KOH and certain of the carbowax/KOH systems appeared as effective as DS2 in decontamination of HD at ambient temperature.

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DEVELOPMENT OF PACKAGE DECONTAMINATING SYSTEM

I. OBJECTIVES

The objective of this research program is to improve the present operational package decontaminating system, DS2. An improved system, and the most desirable, would include a reduction of components, toxicity, and fuming while improving low temperature viscosity and reactivity.

In addition to meeting these improvements, an improved system must meet the following specifications:

- flash point greater than 80°F
- viscosity less than 400 cp at -25°F
- good storage stability
- sprayable in the M11 1.5-qt apparatus
- easy to formulate on a large scale

With regard to reactivity, the decontaminating system must be capable of destroying 2-4% mustard, 10% G and V agents in 5-minutes at ambient temperatures.

II. TECHNICAL BACKGROUND

In the past, most of the effort has been confined to improving DS2 by Edisonian substitution of the components in the DS2 formulation. In the accepted formulation, the substitution method was necessitated due to a limited knowledge of the functions of the components in an agent - DS2 reaction, especially that of the amine. A host of amines, bases and solvents have been tested, in various combinations, in the attempt to improve DS2. The areas which have been considered to be of the greatest importance include a reduction in the number of components, reduced toxicity, and fuming, while improving low temperature viscosity and reactivity.

The present operational decontaminant DS2 has the following composition:

- 70% diethylenetriamine (DETA)
- 28% methyl cellosolve
- 2% sodium hydroxide

DS2 is a unique combination of a solvent, a reactant, and a promoter. The anomalies in the reactivity and general behavior

of DS2 are part of its uniqueness. Ordinarily a solution of an amine, a strong base, and a solvent (alcohol or other) is a simple system and its reactions can be predicted with some accuracy and assurance. However, the rate of reaction of DS2 with HD is much faster than would be predicted, suggesting that DS2 is not merely a solution of a strong base in a moderately polar solvent.

A. Amine

1. Function

The function of the amine in DS2 has been uncertain since its inception in the 1950's. Although, the amine does not react, it has been shown that the percent NH_2 present in the molecule, is directly proportional to the amount of HD destroyed during an HD/decontaminant reaction (figure 1). The first indication of the true function of the amine emerged from the combined application of aprotic chemistry and theoretical mechanistic organic chemistry to the DS2 and DS2T (TREN/MEA substituted for DETA in DS2) data. These data led to the development of the clathration theory, i.e., the amine in DS2 functions as a clathrating agent for the cation (Na^+) (figure 2) preventing ion-pairing with the anion (OH^-). As the strength of clathrating agent increases, ion-pair separation becomes more efficient resulting in a significant increase (orders of magnitude ?) in base strength. Clathration increases with the concentration of NH_2 groups. Thus, it could be predicted that the order of reactivity of hydrazine, ethylenediamine, TREN, and DETA decrease respectively in HD/decontaminant reactions. This supposition has been proved experimentally (figure 1).¹

The amine probably assumes a stereochemical configuration (figure 3) similar to triethylamine in the absence of an attractive force such as a cation; i.e., two of the groups are back and one group projects into the region normally assigned to the unshared pair of electrons.

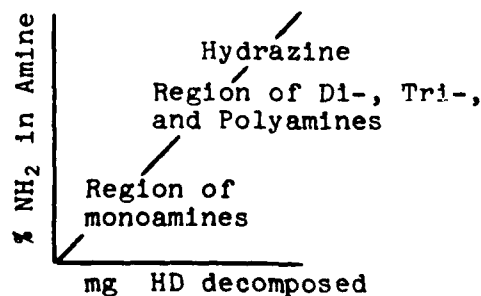


Figure 1. Effectiveness of Amines in HD Decomposition

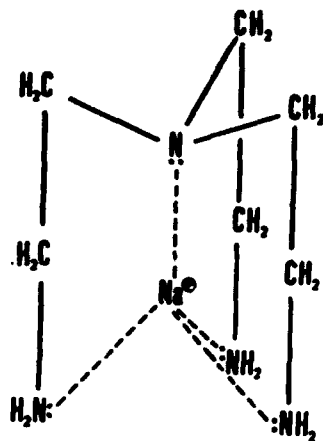


Figure 2. Sodium/TREN Clathrate

As the cation approaches the polyamine, it is attracted to the unshared pairs of electrons on the nitrogen atoms, which are simultaneously attracted to the cation. This forces the molecule into an umbrella-like or cage configuration in which the unshared pairs of electrons are pi-bonded to the cation (figure 2).

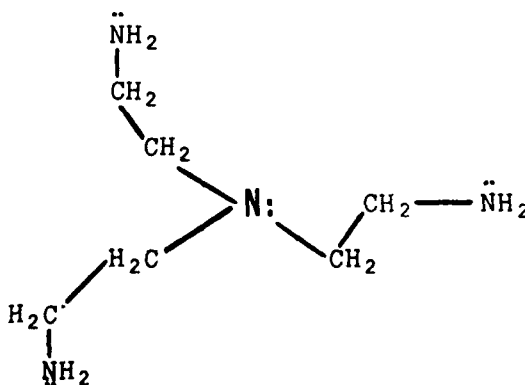


Figure 3. Stereochemical Configuration of TREN

2. Basicity and Concentration

The need for the high concentration of the amine in DS2 has not been apparent, but it is known¹ that an optimized formulation of DS2 must contain at least 65% of the amine component. There is a drastic reduction in the amount of agent destroyed below this concentration. This phenomenon can be explained qualitatively by the theory of highly basic media, i.e., on the basis of the H_- function (basicity of the solvent) of aprotic or aprotic-type solvents.

There is no question that the basicity of the solvent is of prime importance in highly basic media. The higher the H_- of the medium, the more basic the final system. This is the reason that OH^\ominus is a much stronger base in t-butanol ($H_- = 17$) than it is in methanol ($H_- = 10.6$) or ethanol ($H_- = 12.6$). This effect becomes even more pronounced in dipolar aprotics ($H_- = 26$ for OH^\ominus in DMSO, $H_- = 30$ for H^\ominus in DMSO; compare $H_- = 14$ for aqueous 1M NaOH). Ethoxide ion is 12 - 14 powers of ten stronger a base in DMSO than it is in alcohol. This is because ion association (pairing) takes place in alcohols and water even at low concentrations of base. Additionally, there is a high degree of hydration (solvation) in water (alcohols).

Hydroxide ion is known to be the strongest base that can exist in water, but it is so extensively hydrated that it is inhibited to the point of being a "weak base." This can be seen by comparison of OH^\ominus in water and dipolar aprotic solvents. For example if DMSO is added to a 0.01 M solution of OH^\ominus in water, the H_- gradually increases from a value of 12 in the aqueous solution ($H_- = 12$ for aqueous 0.01 M OH^\ominus) to a value of 26 in 99.5 mole percent DMSO. This is explained by the fact that anions of small size and localized charge (OH^\ominus for example) are much stronger bases in aprotics because there is little or no hydrogen bonding with the solvent. They are less solvated than in aqueous media resulting in increased hydroxide ion activity. In addition the aprotic solvent prevents ion-pairing of anion with the cation.

Based on the above facts, DS2 is at least a semi- aprotic, if not an aprotic, system. The amine can be logically considered an aprotic-type solvent in DS2 because it does clathrate (complex with or chelate) the cation and it is a strongly basic medium. The OH^\ominus is solvated to a very low degree, and it is not ion-paired; as a result it is a powerful base. It now becomes obvious why dilution of the amine with alcohol or other hydrogen-bonding, non- aprotic solvents below a concentration of 65% is critical. The amine must therefore be present in high enough concentration to overcome the opposing effects of the alcohol while still maintaining an aprotic-type system.

B. Function of the Base and Alcohol

Although the functions of the base and alcohol in DS2 reactions have long been known, the actual mechanisms through which they occur has been merely speculative. These mechanisms can now be clarified as a result of the identification of the role of the amine.

The base is the primary decontaminating constituent in DS2. As a result of the amine, its strength is increased several orders of magnitude to a level equivalent to a "super base."

The alcohol (methyl cellosolve) functions primarily as an extender, i.e., it is a mutual solvent for the base, amine, and agent. There is a definite possibility that the alcohol may function as more than just an extender, i.e., it could also aid in the dehydrohalogenation of HD. Dehydrohalogenation is a characteristic reaction of alkyl halides containing β -hydrogens in alcoholic caustic.

III. APPROACH

It has been generally agreed that an improved decontaminant definitely necessitates a new approach. Most of the effort has been confined to substitution of the DS2 components. The probability is very low of developing a better decontaminant than DS2 from an amine, a strong base, and a solvent. However, it may be possible to effect some improvement of DS2 by using different permutations and combinations of amines, alcohols, and bases, but significant improvement will be realized only by developing new and different formulations. This can come about only by studying the basic chemistry and mechanisms of decontamination.

Our approach is primarily based upon our mechanistic organic chemical theory of the role of the amine in DS2. The amine is of particular interest because it comprises 70% of the mixture, and it is the primary factor in many of the problems encountered with DS2.

IV. EXPERIMENTAL

A. Analytical

1. Gas-Liquid Chromatograph

A Loenco Model 160 gas-liquid chromatograph has been employed for the qualitative analysis of HD in decontaminant reactions. Past experience has shown that sufficiently reliable data, over a range of concentrations, can be obtained using this method.

The conditions for analysis of HD using the Loenco Model 160 gas chromatograph are:

Column: Stainless steel (1/4 in. OD x 4 ft length)
Column Material: 5% XE60 on 60/80 mesh Chromosorb G
Gas Flow: He at 60 ml/min
Detector Current: 175 ma
Injection Port Temperature: 275°C
Column Temperature: Program at 10°C/min (100° to 200°C)
Detector Temperature: 275°C
Sample Size: 10 µl
Attenuation: 2

Decontamination studies are conducted by quenching (diluting) 5 g (~5 ml) samples of 2.5% HD in decontaminant with methyl cellosolve to a final volume of 50 ml. This procedure is followed by injection of 10 µl samples into the chromatograph. Samples (5 g) of 2.5% HD in DS2 at ambient are analyzed at appropriate times after quenching with 45 ml of methyl cellosolve.

The GLC method will be used throughout the program for screening candidate formulations.

2. DB-3 Tube Technique

This method is the most reliable indicator for detecting trace quantities of HD. This method has been thoroughly examined and is consistent when comparing its results with those of the glc. This method will be used as the ultimate test indicating almost total destruction of HD (99.96%).

The DB-3 tube test is performed according to the following procedure:

The vapor above a sample containing HD is aspirated through the DB-3 tube for one minute at a flow rate of 1 liter per minute; the tube is heated for 5 min. at 100°C, and allowed to cool to room temperature; the color is developed by the addition of a few drops of 10% aqueous sodium hydroxide. The absence of color indicates that <0.5% HD remains.

3. Calibration Standards

In an earlier contract (DAAA15-70-C-0050) it was observed that a second peak developed in the chromatograms after the standard HD samples were stored a short time in the refrigerator. This was linked to impurities in the cellosolve and we have surmised that this second peak (on the high temperature side of HD) may be HD sulfoxide which could be formed from

the peroxides present in cellosolve. Accordingly, three standard samples were made and stored under different conditions in an attempt to follow formation of this second peak. They are: (1) chromatquality cellosolve plus HD stored under nitrogen in the refrigerator; (2) fresh commercial cellosolve plus HD stored in the refrigerator under air; and (3) one-year-old commercial cellosolve (stored in a tightly-sealed bottle) plus HD stored in a loosely-capped bottle at room temperature. In addition, two samples containing peroxide were prepared and tested. The two formulations (numbers 4 and 5 Table I) were based on a known literature reaction of HD and hydrogen peroxide. The results are shown in Table I.

Table I

CALIBRATION STANDARDS AND PEROXIDE FORMULATIONS		
No.	Formulation	% HD ⁽¹⁾ Destroyed (glc Ambient-1 wk)
1	0.03g HD/25 ml MC	51.5
2	0.03g HD/25 ml MC	51.7
3	0.03g HD/25 ml MC	No change
		<u>% HD Destroyed (glc Ambient-1 min)</u>
4	4.00 ml Acetic acid 0.9 ml 30% H ₂ O ₂ 0.1 ml HD 45 ml MC	41.3
5	1.00 ml Acetic acid 0.23 ml H ₂ O ₂ 0.32 ml HD 48.5 ml MC	0

(1) 0.125 g HD: 4.9 ml decontaminant

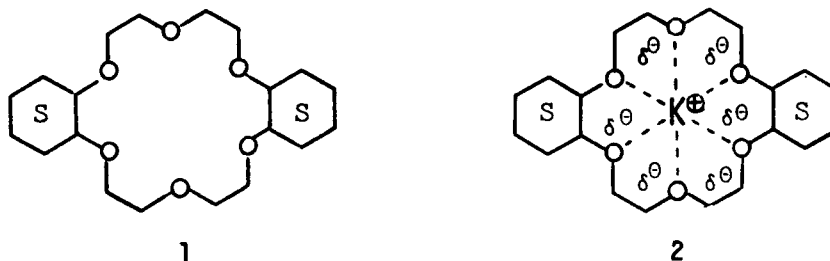
Whereas peroxide does effect destruction of HD, it is apparently not responsible for the second peak previously observed in the chromatograms because none were detected in these experiments. It is obvious that the purity of the MC is important because the concentration of HD in the chromatquality MC was unchanged. Additionally, neither age nor refrigeration appears to be significant in stored HD/MC standards. Further studies will be discontinued since no valid conclusions can be drawn regarding the second peak. Fresh calibration standards will be prepared for each series of formulations.

B. Formulation Studies

The first quarter ended with the preparation of various decontaminant systems utilizing clathrating agents, alkali halide/aprotics, and other potential dehydrohalogenators.

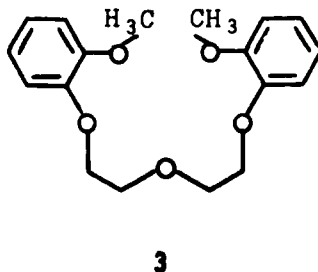
1. Clathrating Agents

Theoretically, effective decontaminants can be produced by substituting chosen clathrating agents in DS2. A number of DS2-type formulations containing clathrating agents were examined. These included a crown ether (dicyclohexyl-18-crown-6), methoxy polyethylene glycols (Carbowax "50" series), and polyethylene glycols (Carbowax 200 series). The crown ether (compound 1) was chosen on the basis of its known clathrating ability. An example of the clathrate product, indicating the position of the cation, is shown pictorially in compound 2. Accordingly, dicyclohexyl-18-crown-6 (compound 1) was



substituted for DETA in DS2 at two levels of concentration (Table II). Formulation 1 was prepared on a molar basis, i.e., equimolar concentrations of crown ether and potassium hydroxide. Formulation 2 was prepared using concentration equivalent to those in DS-2. Formulation number 3 was prepared by substituting DETA for the crown ether as a means of comparison; DS2 is also included for comparison.

It has been observed that open-chain macrocyclic polyethers (dibenzopentaoxapentadecadienes, compound 3) strongly bind sodium and potassium ions. This



immediately suggested the methoxy polyethylene glycols (Carbowax "50" series) which are aliphatic "straight-chain" analogs of compound 2. Compound 3 has 15 atoms in its chain and Carbowax 350, the lowest member available in the "50" series, has 24 atoms in its chain ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_3$; where $x = \sim 7$). As a result, a number of formulations (numbers 5-10, Table II) were prepared and tested at various levels of concentration. Finally, polyethylene glycol 200 (number 11, Table II), the next obvious substitution, was examined.

Table II

CLATHRATING AGENTS/BASE/SOLVENT FORMULATIONS

No.	Formulation	% HD ⁽¹⁾ Destroyed (glc Ambient-1 min)
1	13% $\text{C}_{20}\text{H}_{36}\text{O}_6$ -84.6% MC-2.4% KOH	49.2
2	68% $\text{C}_{20}\text{H}_{36}\text{O}_6$ -28.5% MC-3.5% KOH	100
3	13.7% DETA-84.4% MC-1.9% KOH	47.6
4	DS2	100
5	95% Carbowax 350-5% KOH	100
6	70% Carbowax 350-26% MC-4% KOH	90.5
7	70.2% Carbowax 350-26.1% MC-3.7% $\text{Ca}(\text{OH})_2$	Not tested ⁽²⁾
8	37.1% Carbowax 350-55.1% MC- 7.8% $\text{Ca}(\text{OH})_2$	Not tested ⁽²⁾
9	70% Carbowax 550-26% MC-4% KOH	100
10	35% Carbowax 550-61% MC-4% KOH	85.7
11	70% Carbowax 200-26% MC-4% KOH	0

(1) 0.125 g HD: 4.9 ml decontaminant

(2) $\text{Ca}(\text{OH})_2$ was insoluble

It is evident when comparing the crown ether formulations with the DS2-type formulations (numbers 1-4) that the crown ether is at least equivalent to, and probably better than DETA in a decontaminating formulation. The data also indicates that the open-chain polyethylene glycols with methoxy end-groups (Carbowax "50" series) are nearly equivalent, and in one case (number 9) is equivalent, to the crown ethers. Carbowax

200 is ineffective in a DS2-type formulation (number 11). This is not surprising due to its short chain length and open OH-groups. However this data definitely does not eliminate the longer chain polyethylene glycols (Carbowax 300, 400 and 600).

2. Alkali Halide/Aprotic Systems

Formulations 1 - 10 (Table III) are an expansion of the dehydrohalogenation concept. This concept is based upon the fact that lithium chloride in DMF is used commercially to dehydrohalogenate pvc. The action of lithium chloride in DMF is due to the chloride ion (Cl^-) which is a strong base in aprotic solvents and is the actual dehydrohalogenating agent. It follows that this should be directly applicable to HD since HD is considered to be destroyed by removal of its chlorine. Although the pvc reaction is conducted at elevated temperatures, there was excellent probability that an alkali halide/aprotic system would react with HD at room temperature since the chlorine in HD is several orders of magnitude more reactive than those in pvc. This hypothesis was based on the fact that the highly reactive chlorine in HD would compensate for the difference in the amount of energy required for the proposed reaction. Although sodium, potassium, and ammonium chloride and lithium bromide are not used (commercially) in DMF, the probability existed that these compounds could be equivalent to lithium chloride in an aprotic solvent. In addition other aprotic solvents were substituted for DMF. Formulations 11 - 14 (Table III) were prepared and tested based on the fact that each of these compounds is known to react with organic chlorine.

Examination of the formulations in Table III show that the alkali halide/aprotic systems were ineffectual dehydrohalogenating agents for HD at ambient temperature. The exact reason for the inactivity of formulations 1 - 10 is unknown. These reactions are apparently temperature-dependent; the same appears to be true for formulations 11 - 14.

V. FUTURE PLANS

Immediate plans call for studying new samples of Carbowax 200, 300, 400, 600 and 350 at various levels of concentration. Additionally, lithium diethylamide and magnesium ethoxide, powerful E2 promoters, will be tested in addition to other very strong bases, with and without clathrating agents present. For purposes of comparison, polyethyleneimine, the nitrogen analog of the Carbowaxes, will be tested.

Long range plans call for the identification of a two-component, clathrating agent and base, and/or three-component system, with a reduction in the clathrating agent, which will meet military specifications.

Table III

VARIOUS BASE/SOLVENT FORMULATIONS

No.	Formulation	% HD ⁽¹⁾ Destroyed (glc Ambient-1 min.)
1	5% LiCl-95% DMF	0
2	5% LiCl-95% DMF @ 50°C	0
3	5% LiCl-95% DMF @ 75°C	0
4	5% NaCl-95% Formamide	28.6
5	5% KCl-95% Formamide	19.0
6	5% NH ₄ Cl-95% Formamide	31.7
7	5% LiBr-95% Formamide	0
8	5% LiBr-95% DMF	4.8
9	5% LiCl-95% THF	14.3
10	5% LiCl-95% Hexamethylphosphoric Triamide	11.1
11	5% Na Acetate-95% MC	0
12	5% Acetanilide-95% MC	0
13	100% [(CH ₃) ₂ N] ₃ P	<6.3
14	10% Thiourea-90% MC	0

(1) 0.125 g HD: 4.9 ml decontaminant

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